LASER INDUCED BREAKDOWN SPECTROSCOPY OF SOILS, ROCKS AND ICE AT SUBZERO TEMPERATURES IN SIMULATED MARTIAN CONDITIONS

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INTRODUCTION

LIBS = Laser Induced Breakdown Spectroscopy

The future missions to Mars of NASA (Mars Science Laboratory) and ESA (ExoMars) will include a robotic rover, and a LIBS instruments to investigate the elemental composition of the Martian surface.

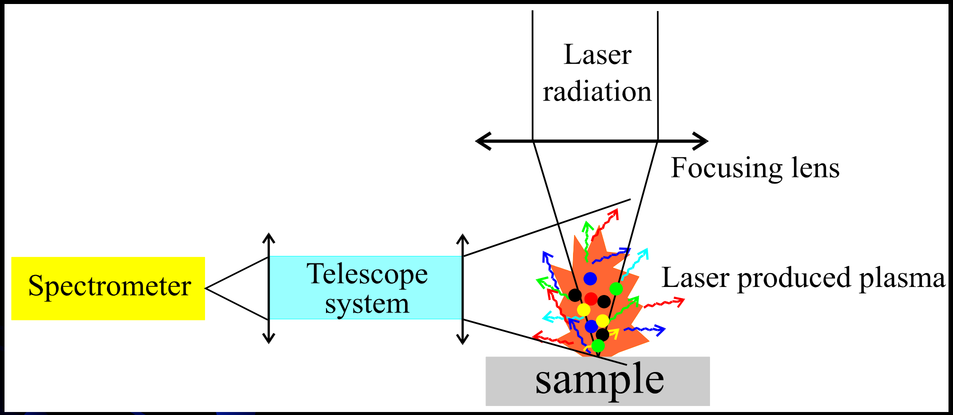
ESA specifies that the LIBS instrument should operate at the temperatures from -60°C to 30°C.

Laser removal of surface debris and ice is also planned in order to analyze under laying material

PRINCLIPLES OF LIBS

LIBS is a powerful tool for rapid, in-situ analyses of solid, liquid or gaseous samples in different surroundings .

A plasma is generated by laser ablation of solid targets or by breakdown in medium (gaseous or liquid). The LIBS plasma contains the elements originally present in the ablated sample layer (or in the excited volume).



Spectrally resolved plasma emission is exploited to determine the elemental sample composition in range from 1 ppm to 100%.

Development of wide range, high-resolution spectrometers, allows for multi-elemental measurements also by applying a single laser shot.

Sample preparation is not required

The measurements are without contact, thus excluding any sample contamination.

The laser pulses can also remove the external surface layers, and elemental distribution at depth can be measured on a small scale (up to a few millimeters).

PREVIOUS LIBS STUDIES FOR MARS

-Calibration on dry samples at room temperature: it was assumed that surface temperature does not influence the signal, being the plasma temperature very high, about 8000 K (CNRS – France, Los Alamos National Lab – USA, ENEA – Italy)

- Measurements of the LIBS signal from on soil/ice mixtures at fixed temperature: the signal decreases with ice content due to its lower absorption (Z. A. Arp, et. la, Appl. Spectrosc. 58, 2004)

-Measurements of ice ablation rates at -30°C and -110°C: the ablation rate was lower for the colder ice, attributed to an increased energy requirement to melt the ice

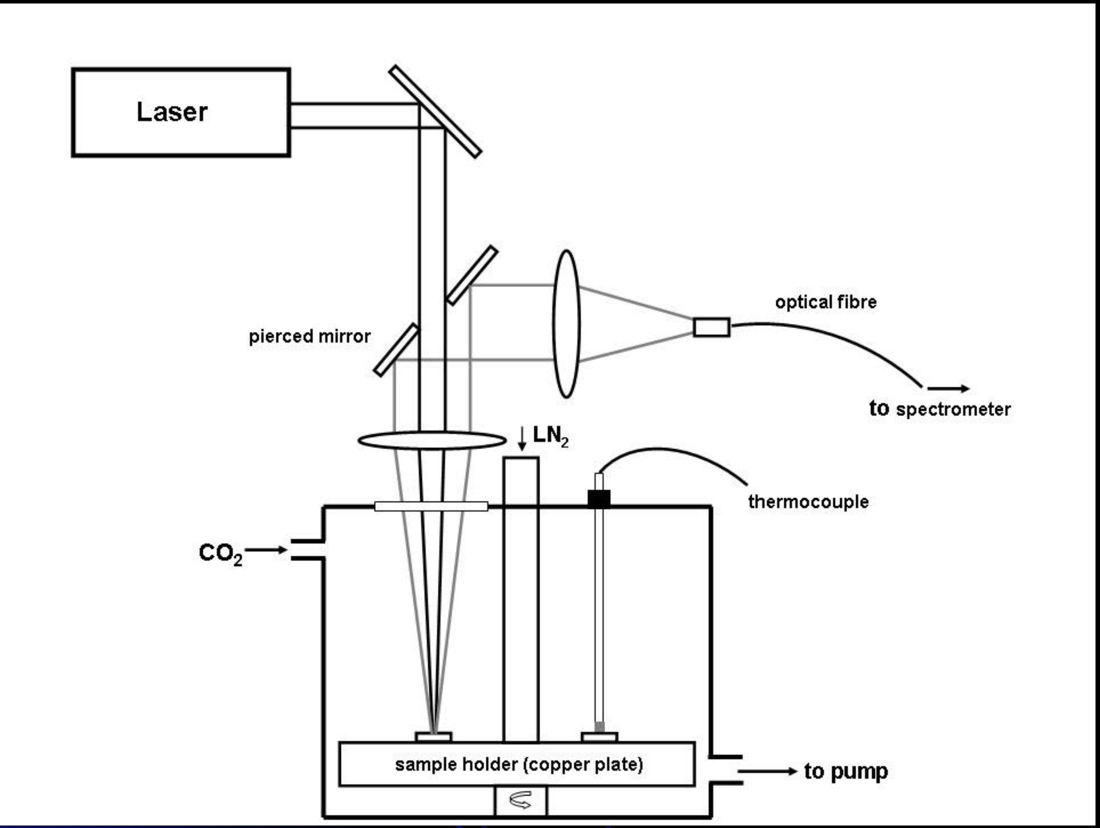
Spectroscopic measurements indicate a presence of water adsorbed by Martian soil, and the water ice presence at higher latitudes.

↓

LIBS ANALYSES SHOULD CONSIDER THE SOILS/ROCKS CONTAINING WATER/ICE AND AT DIFFERENT TEMPERATURES.

EXPERIMENTAL

We studied a behavior of the LIBS signal on soils, rocks and on ice, in simulated Martian atmosphere, as a function of the sample temperature from 25°C to -60°C.



Laser Nd:YAG, 1064 nm, pulse width 8 ns, repetition rate 10 Hz.

Laser energies: 12.5 mJ (14 J/cm^2) and 70 mJ (40 J/cm^2 equivalent to 5 GW/cm^2, initially specified by ESA)

Monochromator 0.55 m, resolution 0.12 nm or better, ICCD detector (gain set to 0).

Acquisition gate 5 μs, gate delay 200 ns (optimized)

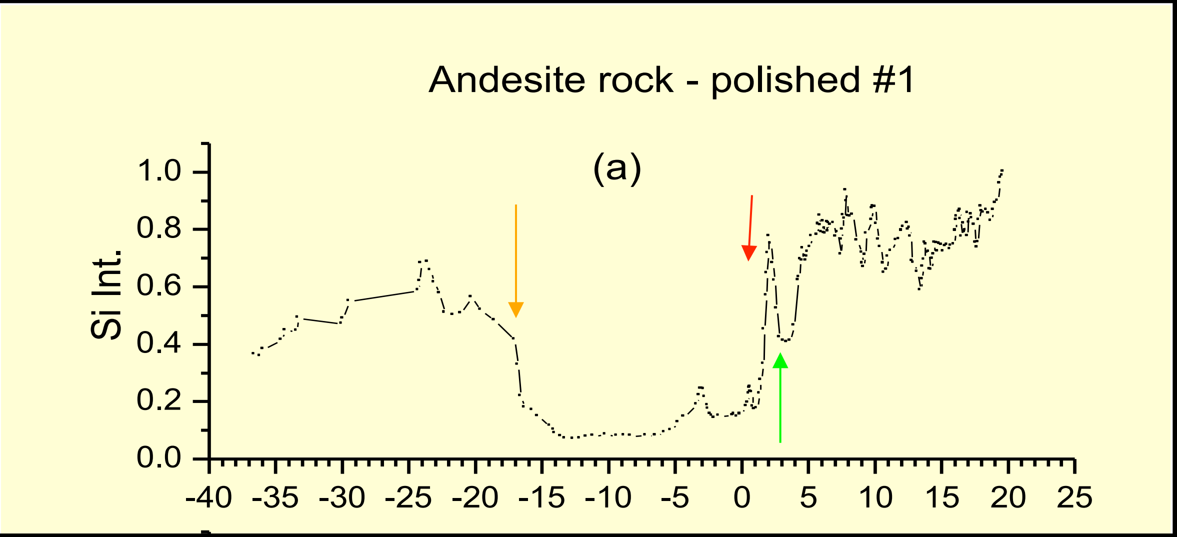
Gas pressure: 7 mbar

Sample holder is cooled by LN. The temperature of the sample surface was measured indirectly, on the same sample type with similar thickness, placed in a contact with a thermocouple

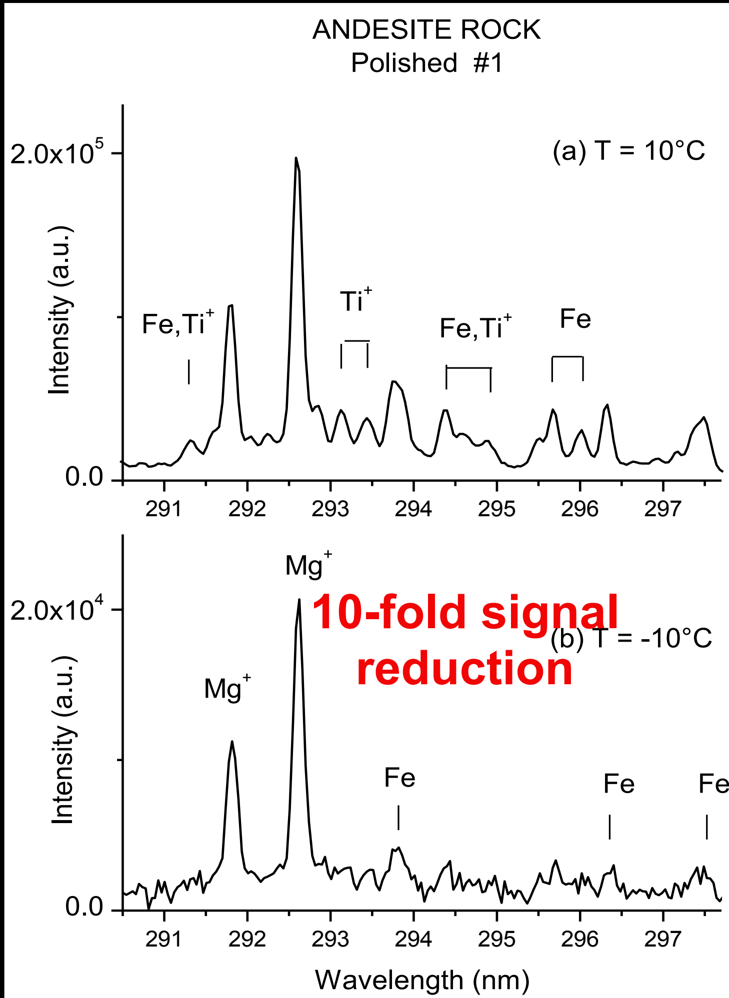
RESULTS – ROCK SAMPLE

Andesite (Eifel region, Germany): the main constituent is silica (about 43%).

1 mbar air (water condensation) + 6 mbar CO_2; cooling



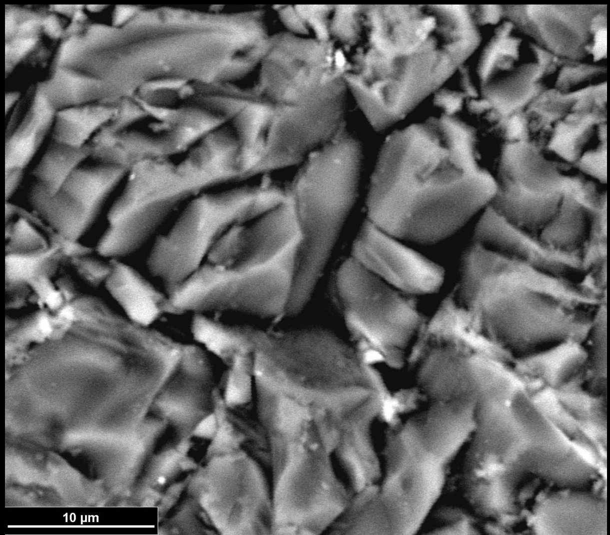
SURPRISE!!!



3°C: close to boiling point

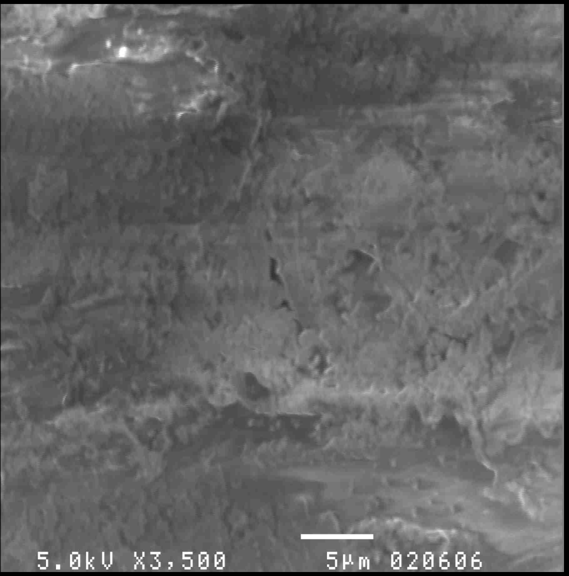
0°C: freezing point

0°C to -17°C: ???

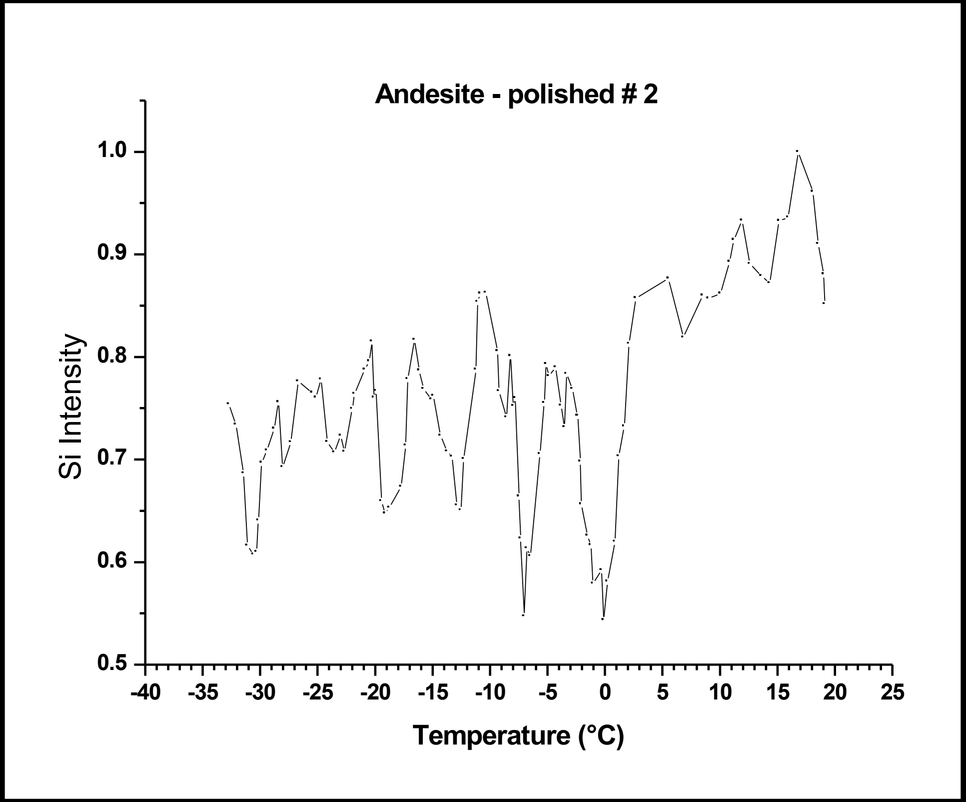


Diamond sintered on bronze, 60-70 μm, cutting wheel

RESULTS – ROCK SAMPLE



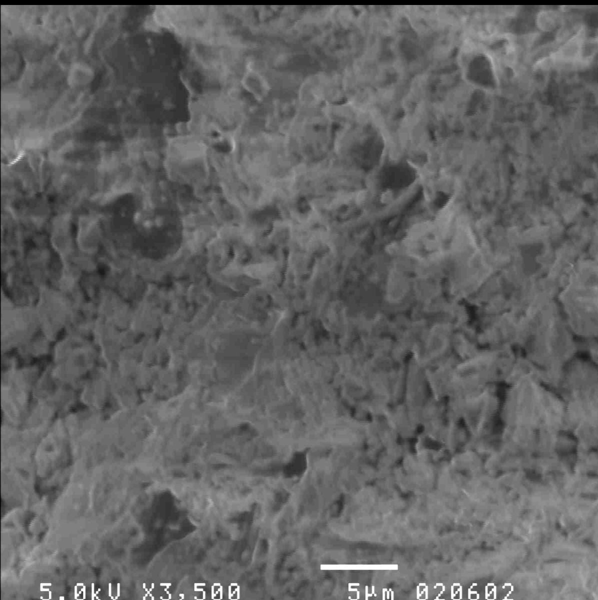
Andesite, treated with emery 140 μm: smaller pores, but large scratches



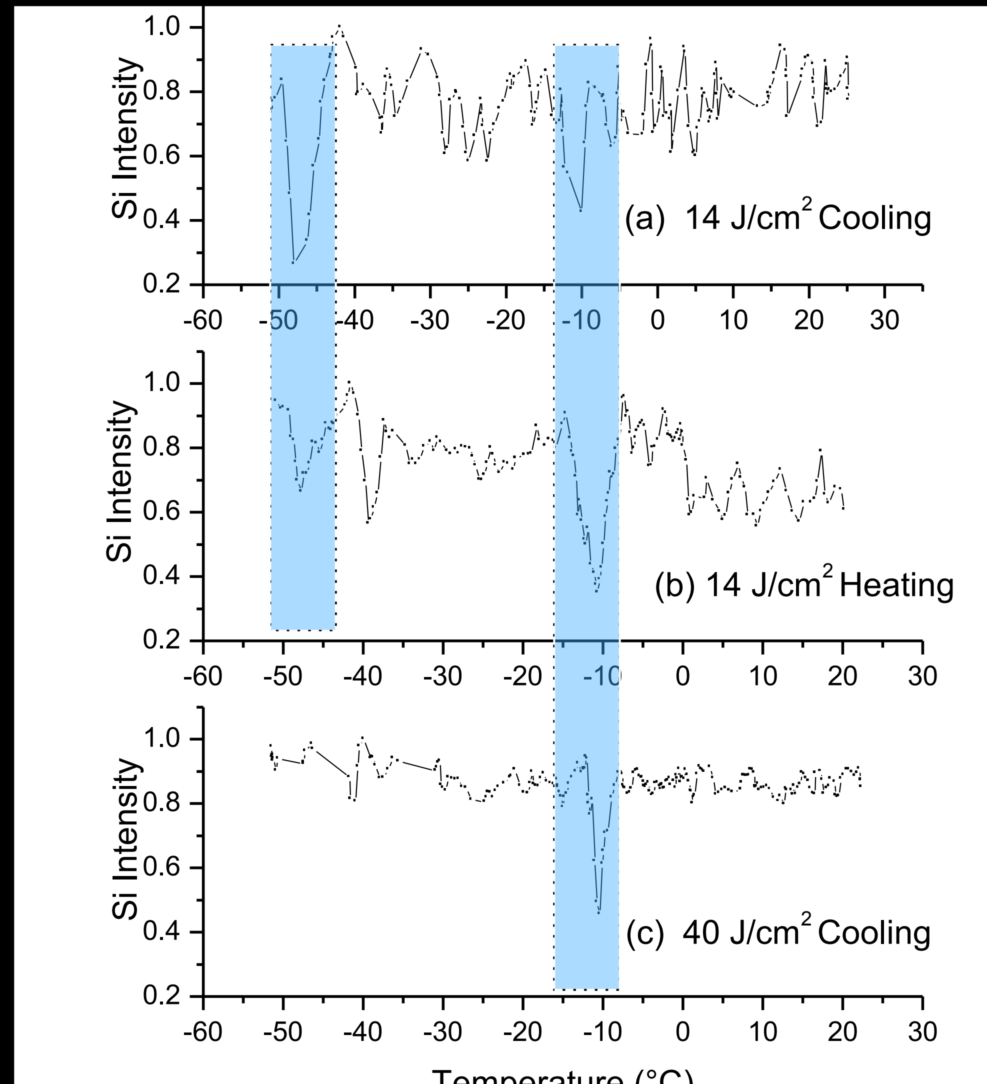
Different smaller negative peaks below 0°C.

Signal drop close to 0°C

RESULTS – ROCK SAMPLE



Diamon polishing 30 µm:
smaller pores, no scratches



Always negative peak close to -10°C

Very weak depression close to 0°C.

Deep negative peak close to -50°C
(for well T resolved measurements)

WHAT HAPPENS BELOW 0°C?

Literature: water/ice transformations, geology, cryobiology, mesoporous materials etc…, <u>above triple point (pressure 6 mbar)</u>

At 0°C free water (surface, large scratches and pores) transforms to normal, hexagonal ice

By careful cooling, free water can be supercooled down to -40°C, so-called temperature of homogeneous nucleation

Inside small pores, water freezes into defective cubic ice, for lower pore diameter - lower is freezing temperature

At corrugated surfaces, supercooled water can exist down to – 80°C!

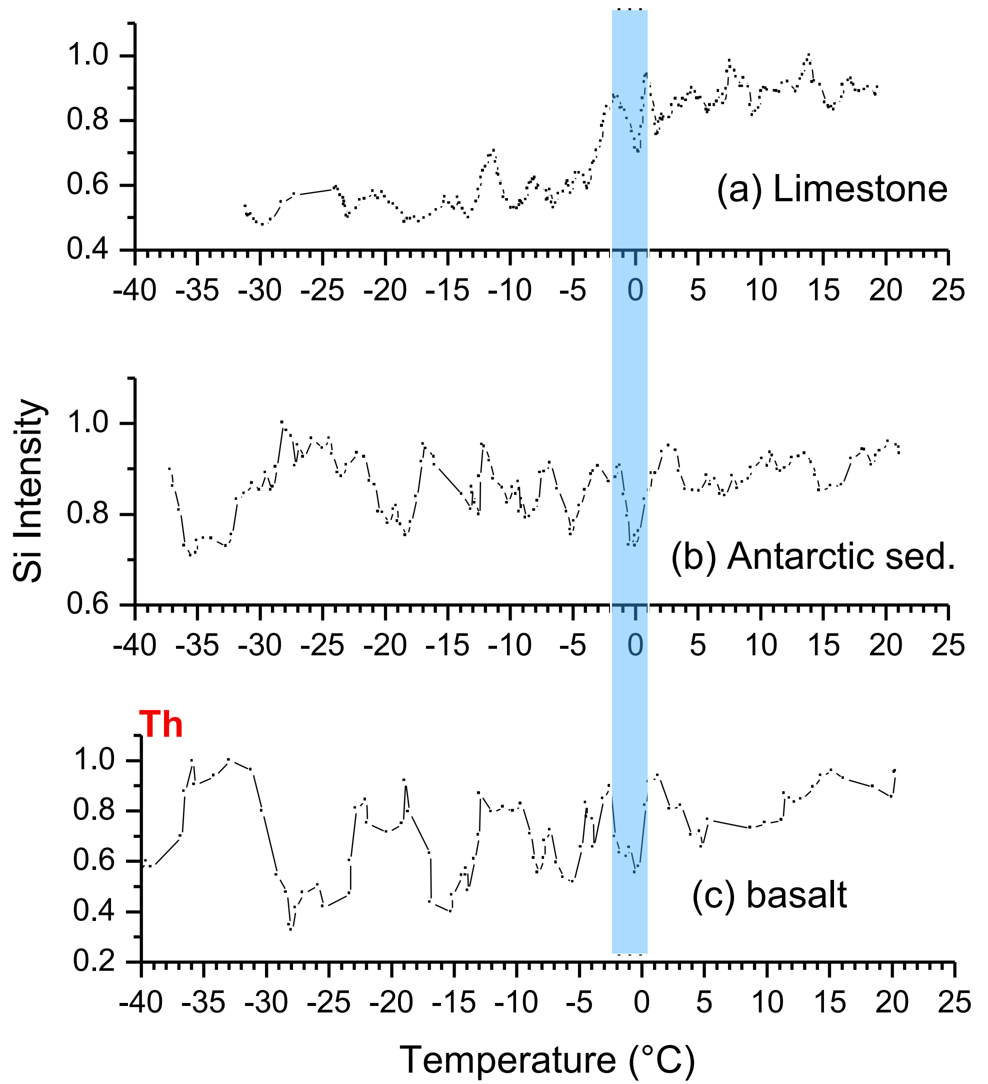
Close to -50°C, supercooled water changes its thermodynamical properties – a transition to low density amorphous structure is hypothesized

The fraction of unfrozen water below 0°C depends on sizes and shapes of the pores and grains, then on impurity concentrations and on local environment (pressure and temperature).

LIBS SIGNAL DEPENDS ON THE SURFACE ROUGHNESS AND GRAIN SIZES. IT DROPS CLOSE TO THE PHASE TRANSITION TEMPERATURES!

RESULTS – SOIL SAMPLES

Powder samples pressed into pellets, cooling cycle

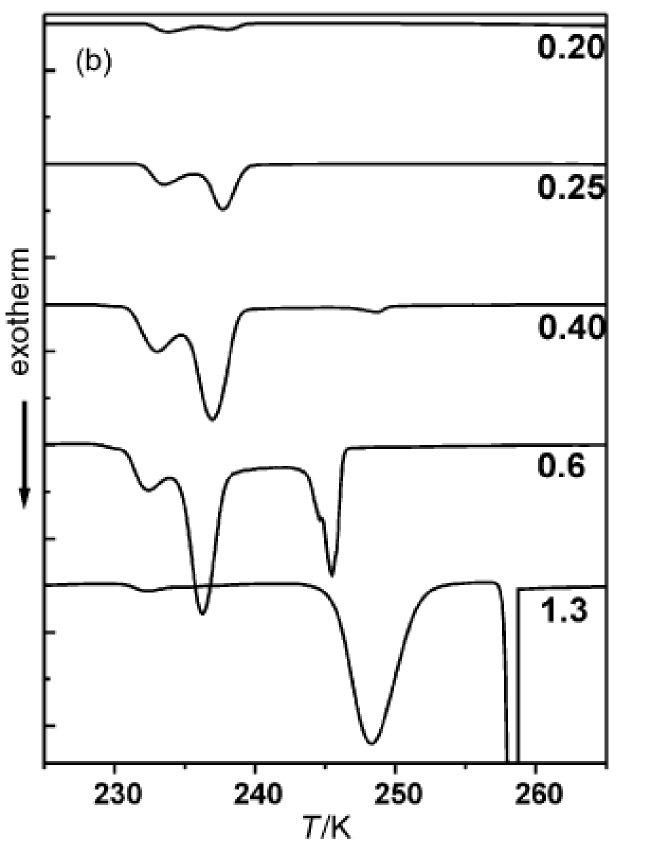


Different negative peaks below 0°C.

Signal drop close to 0°C

Signal drop at Th (homogeneous nucleation)

COMPARISON LIBS - DSC



Mesoporous silica, different degrees of pore fillings

Schreiber A., et al,, I. Phys. Chem. Chem. Phys. 3 (2001) 1185-1195.

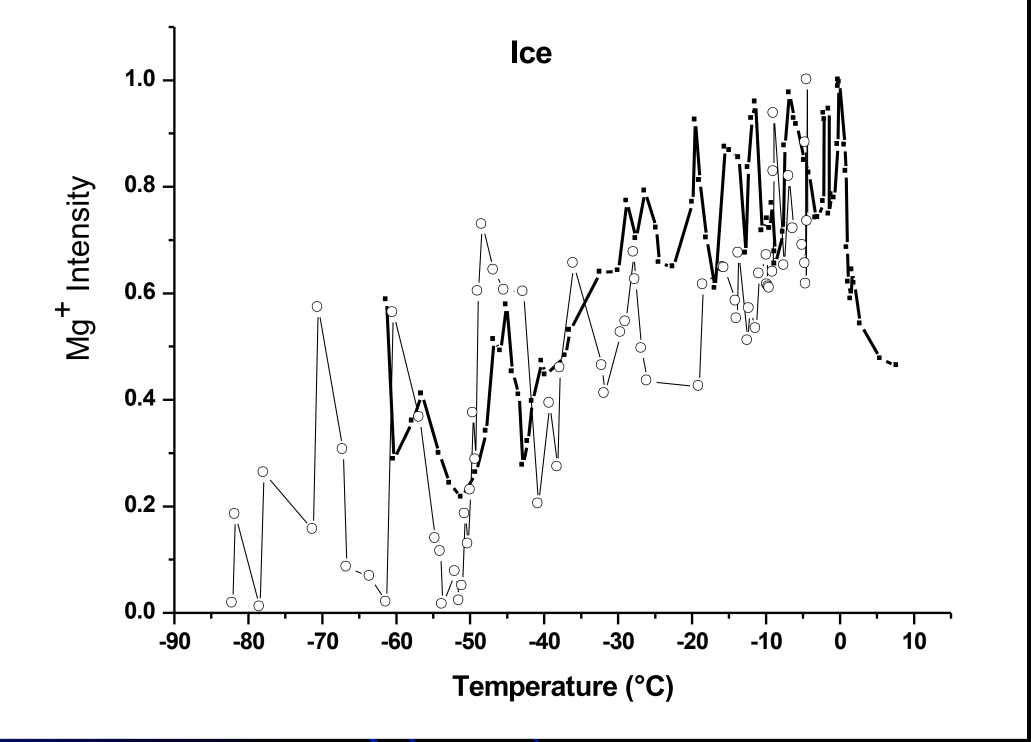
The obtained LIBS signal dependency on the sample temperature is quite similar to the results reported by Differential Scanning Calorimetry (DSC) for mesoporous materials. In such measurements, the phase transition is characterized by a discontinuity of the measured thermal conductivity due to latent heat of transition.

In the case of laser ablation, the absorbed laser energy by coexisting ice-water phase seems to be first used to complete the transition of the ice to water and only then evaporate (ablate) the liquid.

<u>At pressures below 6 mbar, we did not observe negative LIBS peaks at subzero temperatures (direct ice sublimation). The LIBS signal oscillation below 0°C is caused by supercooled water!</u>

RESULTS – ICE SAMPLES

The ice samples: milli-Q water + $MgSO_4$ (50 mg/l of Mg). Mg has strong emission lines and normally is present in the soils and rocks. These samples were slowly cooled down below 0°C in order to obtain homogeneous ice nucleation and consequently a smooth surface. Heating cycle



At -50°C and some lower T, signal drops even 100 times!

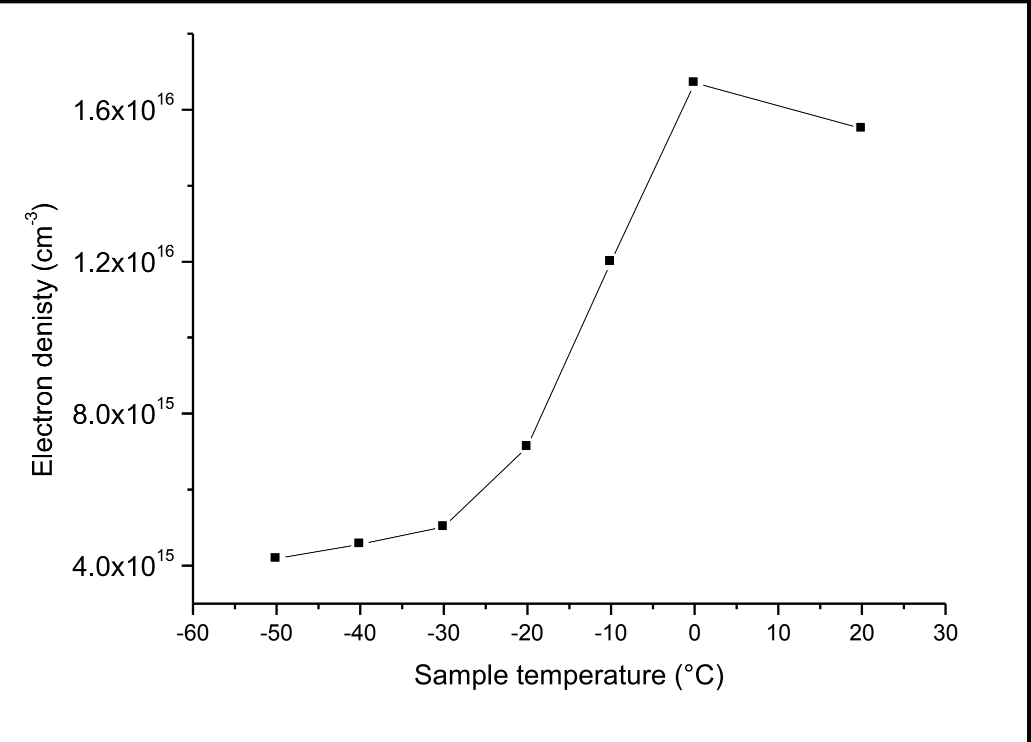
Low ablation rates – can compromise the ice removal by laser

Progressive signal increase towards 0°C: reduced thermal conductivity and the ice premelting. The craters become larger than the laser spot size – easier ice ablation

Bulk ice ablation below -40°C should be further studied.

RESULTS – PLASMA PARAMETERS

Measurements on a reference basalt sample: 20 laser, the sample was first sprayed with tap water and cooled down to – 50°C, 7 mbar of CO_2, applying 14 J/cm^2 or 40 J/cm^2.



Higher energy: T= (7500 +/-500 K)

Electron density: 4-fold decrease with the sample temperature.

Between -10°C and -30°C, Mg/Mg+ ratio in plasma changes 2 times!

In the calibration and quantitative analyses at variable sample temperatures, the plasma parameters must be included!

Lower energy: we observed a deviation from LTE (Local thermal Equilibrium), less favorable for quantitative analyses

CONLUSIONS

For the first time, a behavior of LIBS signal as a function of the sample temperature below 0°C was studied on soil, rock and ice samples.

LIBS signal from moist samples, at pressures above 6 mbar, shows strong temperature dependence below 0°C. We attribute such a signal behavior to the phase transitions of supercooled water, whose amount and the freezing temperature depends on the material pore/grain sizes.

In proximity of the phase transition temperatures, on soils/rocks we measured the signal depression up to an order of magnitude, with consequences on the LIBS analytical capability

Hexagonal ice on the sample surface can be removed by laser ablation. The same type of ice exists also inside larger pores, causing a signal drop at 0°C.

The measurements near -50 °C produced the signal reduction up to 80% on the rock samples and for factor 100 on the ice.

The measured plasma electron density strongly depends on the sample temperature.

RECEPY FOR LIBS AT VARIABLE TEMPERATURES?

(For ice and for soils containing ice/water, at pressures above triple point (6 mbar)

LIBS analysis, also in Martian conditions, should exclude the operation close to the points of the known phase transitions of water and ice, i.e. around 0°C, - 40°C and -50°C.

Higher temperatures are more favorable for the ice removal by laser.

Larger focal spot size would allow for interaction with a wider range of pore dimensions present on the natural samples. This reduces the signal variation with the temperature, caused by the phase transitions dependent on the pore size.

The calibration procedure should take into account the plasma parameters, being the measured plasma electron density strongly dependent on the sample temperature.

For higher energy densities on a sample, smaller is the plasma deviation from LTE and the necessary corrections for variable plasma parameters are more affordable.

ACKNOWLEDGMENTS

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